

Express Mail #EL822581508US
Application No.: PCT/RU99/00037

VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Specification:

On Page 7, Table 1, Column 4, line 1, has been amended as follows:

Table 1

No.	Composition	Propane activation temperature, °C	Propane to hydrogen ratio	Tungsten hexafluoride to hydrogen ratio
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On Page 14, Paragraph 3, Example 5, has been amended as follows:

The construction material thus obtained with [copper] tool steel with a layer of nickel as the base material has a composite coating with an internal tungsten (W) layer of thickness 1.3 μm and an external layer of W_2C of thickness 9.1 μm . The microhardness of the coating is 2800 kG/mm^2 .

On Page 22, Paragraph 3, Example 21, has been amended as follows:

The construction material thus obtained with tool steel R6M5 as the base material and an intermediate nickel layer 8 μm thick has a composite coating with 11 alternating layers of W and W_{12}C both with thickness 5 μm at a ratio of thicknesses [1:11] 1:1 and total thickness of the composite coating 110 μm . The average microhardness of the coating is 2550 kG/mm^2 .

In the Claims:

Claims 66 and 90 have been canceled.

Claims 8-50, 57-65, 67, 69-75 and 87-89 have been amended as follows:

8. -(Amended) Coating, [*characterised*] characterized in that it contains:

- an internal layer consisting of tungsten deposited on a substrate;
- and an external layer deposited on the said internal layer and containing tungsten carbide

in accordance with claim[s] 1[-6].

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9. (Amended) Coating in accordance with claim 6, ~~[characterised]~~ characterized in that its outer layer additionally contains a mixture of at least two tungsten carbides alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possible with fluorocarbon compositions with carbon content up to 15 wt% and fluorine content up to 0.5 wt% [in accordance with claim 7].

10. (Amended) Coating in accordance with claim[s] 8[or 9], ~~[characterised]~~ characterized in that its outer layer additionally contains tungsten.

11. (Amended) Coating in accordance with claim[s] 8[or 9], ~~[characterised]~~ characterized in that its outer layer additionally contains carbon.

12. (Amended) Coating in accordance with any of claim[s] 8[to 11], ~~[characterised]~~ characterized in that its internal layer has a thickness of 0.5-300 μm and its outer layer has a thickness of 0.5-300 μm , with the ratio of thicknesses of the internal and external layers ranging from 1:1 to 1:600.

13. (Amended) Process for producing tungsten carbides by chemical vapour deposition on a heated substrate using a mixture of gases including tungsten hexafluoride, hydrogen, a carbon-containing gas and, optionally, an inert gas, ~~[characterised]~~ characterized in that the carbon-containing gas is thermally activated beforehand by heating to temperature 500-850°C.

14. (Amended) Process in accordance with claim 13, ~~[characterised]~~ characterized in that the said carbon-containing gas is propane.

15. (Amended) Process in accordance with claim[s] 13[or 14], ~~[characterised]~~ characterized in that it is performed at a pressure of 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

16. (Amended) Process in accordance with claim 15, ~~[characterised]~~ characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 1.0-1.5 and ratio of tungsten hexafluoride to hydrogen 0.08-0.10, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, tungsten monocarbide WC is obtained.

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17. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.75-0.90 and ratio of tungsten hexafluoride to hydrogen 0.06-0.08, and that the carbon-containing gas is heated beforehand to temperature 600-750°C; in this case, tungsten semicarbide W_2C is obtained.

18. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.05-0.55, and that the carbon-containing gas is heated beforehand to temperature 560-720°C; in this case, tungsten subcarbide W_3C is obtained.

19. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.35-0.45 and ratio of tungsten hexafluoride to hydrogen 0.040-0.045, and that the carbon-containing gas is heated beforehand to temperature 500-700°C; in this case, tungsten subcarbide $W_{12}C$ is obtained.

20. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.90-1.00 and ratio of tungsten hexafluoride to hydrogen 0.07-0.09, and that the carbon-containing gas is heated beforehand to temperature 670-790°C; in this case, a mixture of the carbides WC and W_2C is obtained.

21. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.75 and ratio of tungsten hexafluoride to hydrogen 0.055-0.060, and that the carbon-containing gas is heated beforehand to temperature 580-730°C; in this case, a mixture of the carbides W_2C and W_3C is obtained.

22. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-700°C; in this case, a mixture of the carbides W_2C and $W_{12}C$ is obtained.

23. (Amended) Process in accordance with claim 15, [*characterised*] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.45-0.60 and ratio of tungsten hexafluoride to hydrogen 0.045-0.050, and that the carbon-containing gas is heated beforehand to temperature 550-680°C; in this case, a mixture of the carbides W_3C and $W_{12}C$ is obtained.

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24. (Amended) Process in accordance with claim 15, [~~characterised~~] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.65-0.70 and ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-710°C; in this case, a mixture of the carbides W_2C , W_3C and $W_{12}C$ is obtained.

25. (Amended) Process in accordance with claim 15, [~~characterised~~] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.90 and ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, a mixture of the carbide WC and tungsten is obtained.

26. (Amended) Process in accordance with claim 15, [~~characterised~~] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.90 and ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, a mixture of the carbides W_2C and tungsten is obtained.

27. (Amended) Process in accordance with claim 15, [~~characterised~~] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.055-0.070, and that the carbon-containing gas is heated beforehand to temperature 560-700°C; in this case, a mixture of the carbide W_3C and tungsten is obtained.

28. (Amended) Process in accordance with claim 15, [~~characterised~~] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.20-0.35 and ratio of tungsten hexafluoride to hydrogen 0.045-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, a mixture of the carbide $W_{12}C$ and tungsten is obtained.

29. (Amended) Process in accordance with claim 15, [~~characterised~~] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 0.35-0.60 and ratio of tungsten hexafluoride to hydrogen 0.05-0.07, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, a mixture of the carbides W_3C , $W_{12}C$ and tungsten is obtained.

30. (Amended) Process in accordance with claim 15, [~~characterised~~] characterized in that it is performed at a ratio of carbon-containing gas to hydrogen 1.50-1.70 and ratio of tungsten hexafluoride to hydrogen 0.10-0.12, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, a mixture of the carbide WC and carbon is obtained.

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31. (Amended) Process for the deposition of coatings consisting of an internal layer of tungsten and an external layer containing tungsten [subcarbide $W_{12}C$] carbide on substrates, preferably on construction materials and on items made from them, [*characterised*] characterized in that the said process includes the following stages:

- (a) placing the substrate in a chemical [*vapour*] vapor deposition reactor;
- (b) evacuating the reactor;
- (c) heating the said substrate;
- (d) supplying tungsten hexafluoride and hydrogen to the reactor;
- (e) retaining the substrate in the said gaseous medium for the time interval necessary for the formation of the tungsten layer on the substrate;

- (f) in addition to the said tungsten hexafluoride and hydrogen, supplying a previously thermally activated carbon-containing gas to the reactor;

- (g) retaining the substrate in the gaseous medium formed at stage (f) for the time necessary for the formation of the outer layer containing tungsten carbides and mixtures of them with each other, with tungsten or with free carbon.

32. (Amended) Process in accordance with claim 31, [*characterised*] characterized in that it is performed at a reactor pressure of 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

33. (Amended) Process in accordance with claim 31, [*characterised*] characterized in that, before the application of a coating to materials or items made from materials selected from a group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys containing titanium, a coating is applied to them consisting of materials which are chemically resistant to hydrogen fluoride, namely nickel, cobalt, copper, silver, gold, platinum, iridium, tantalum, molybdenum and alloys, compounds and mixtures of these, by electrochemical or chemical [*precipitation*] deposition from aqueous solutions, electrolysis of melts or physical and chemical [*vapour precipitation*] vapor desposition.

34. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 1.00-1.50 and a ratio of tungsten

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hexafluoride to hydrogen 0.08-0.10, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, an external layer containing tungsten monocarbide WC is obtained.

35. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.75-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.06-0.08, and that the carbon-containing gas is heated beforehand to temperature 600-750°C; in this case, an external layer containing tungsten semicarbide W_2C is obtained.

36. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.050-0.055, and that the carbon-containing gas is heated beforehand to temperature 560-720°C; in this case, an external layer containing tungsten subcarbide W_3C is obtained.

37. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.35-0.40 and a ratio of tungsten hexafluoride to hydrogen 0.040-0.045, and that the carbon-containing gas is heated beforehand to temperature 500-700°C; in this case, an external layer containing tungsten monocarbide $W_{12}C$ is obtained.

38. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.90-1.00 and a ratio of tungsten hexafluoride to hydrogen 0.07-0.09, and that the carbon-containing gas is heated beforehand to temperature 670-790°C; in this case, an external layer containing a mixture of the carbides WC and W_2C is obtained.

39. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.75 and a ratio of tungsten hexafluoride to hydrogen 0.055-0.060, and that the carbon-containing gas is heated beforehand to temperature 580-730°C; in this case, an external layer containing a mixture of the carbides W_2C and W_3C is obtained.

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40. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.65-0.70 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-710°C; in this case, an external layer containing a mixture of the carbides W_2C , W_3C and $W_{12}C$ is obtained.

41. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-700°C; in this case, an external layer containing a mixture of the carbides W_2C and $W_{12}C$ is obtained.

42. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.40-0.60 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.050, and that the carbon-containing gas is heated beforehand to temperature 550-680°C; in this case, an external layer containing a mixture of the carbides W_3C and $W_{12}C$ is obtained.

43. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, an external layer containing a mixture of the carbide W_2C and tungsten is obtained.

44. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.055-0.070, and that the carbon-containing gas is heated beforehand to temperature 560-700°C; in this case, an external layer containing a mixture of the carbide W_3C and tungsten is obtained.

45. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.35-0.60 and a ratio of tungsten hexafluoride to hydrogen 0.050-0.070, and that the carbon-containing gas is heated beforehand to

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temperature 500-690°C; in this case, an external layer containing a mixture of the carbides W_3C and $W_{12}C$ with tungsten is obtained.

46. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.20-0.35 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, an external layer containing a mixture of the carbide $W_{12}C$ and tungsten is obtained.

47. (Amended) Process in accordance with claim 32, [*characterised*] characterized in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, an external layer containing a mixture of the carbide WC and tungsten is obtained.

48. (Amended) Process in accordance with any of claim[s] 31[to 47], [*characterised*] characterized in that the coatings are deposited onto frictional assemblies.

49. (Amended) Process in accordance with any of claim[s] 31[to 47], [*characterised*] characterized in that the coatings are deposited onto forming tools used for processing materials by means of pressing.

50. (Amended) Process in accordance with any of claim[s] 31[to 47], [*characterised*] characterized in that the coatings are deposited onto components and units of machines and mechanisms operating with compressed gases and liquids or other pneumatic or hydraulic systems.

57. (Amended) Material in accordance with claim 56, [*characterised*] characterized in that the external layer of the said coating contains a mixture of the tungsten carbides WC and W_2C [$W_{12}C$].

58. (Amended) Material in accordance with claim 56, [*characterised*] characterized in that the external layer of the said coating contains a mixture of the tungsten carbides W_3C and W_2C .

59. (Amended) Material in accordance with claim 56, [*characterised*] characterized in that the external layer of the said coating contains a mixture of the tungsten carbides W_3C and $W_{12}C$.

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60. (Amended) Material in accordance with claim 56, [*characterised*] characterized in that the external layer of the said coating contains a mixture of the tungsten carbides W_2C and $W_{12}C$.

61. (Amended) Material in accordance with claim 56, [*characterised*] characterized in that the external layer of the said coating contains a mixture of the tungsten carbides W_2C , W_3C and $W_{12}C$.

62. (Amended) Material in accordance with claim[s] 52[-61], [*characterised*] characterized in that the external layer of the said coating additionally contains tungsten.

63. (Amended) Material in accordance with claim[s] 52[-61], [*characterised*] characterized in that the external layer of the said coating additionally contains carbon.

64. (Amended) Material in accordance with claim[s] 52[to 63], [*characterised*] characterized in that the internal layer of the said coating has thickness 0.5-300 μm and the ratio of thicknesses of internal and external layers ranges from 1:1 to 1:600.

65. (Amended) Material according to claim[s] 52[to 64], [*characterised*] characterized in that the said substrate layer adjacent to the coating contains alloys with nickel content exceeding 25 wt%, e.g. Invar, Nichrome, Monel.

67. (Amended) Multilaminar coating made from alternating layers of tungsten and layers containing tungsten carbide in accordance with [any of] claim[s] 1[to 6].

69. (Amended) Multilaminar coating in accordance with claim[s] 67[-68], [*characterised*] characterized in that the thickness of its individual layers ranges from 2 to 10 μm and the ratio of the thicknesses of the alternating layers ranges from 1:1 to 1:5.

70. (Amended) Process for the deposition of multilaminar coatings on substrates, preferably on construction materials and items made from them, consisting of alternating layers of tungsten and layers containing tungsten carbide or mixtures of tungsten carbides with each other, with tungsten or with free carbon, said process-to include the following stages:

- (a) (Amended) placing the substrate in a chemical [vapour] vapor deposition reactor;
- (b) evacuating the reactor;
- (c) heating the said substrate;
- (d) supplying tungsten hexafluoride and hydrogen to the reactor;

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(e) retaining the substrate in the said gaseous medium for the time interval necessary for the formation of the tungsten layer on the substrate;

(f) in addition to the said tungsten hexafluoride and hydrogen, supplying a previously thermally activated carbon-containing gas to the reactor;

(g) retaining the substrate in the gaseous medium formed at stage (f) for the time necessary for the formation of the outer layer containing tungsten carbide or mixtures of tungsten carbides with each other, with tungsten and with free carbon; stages (d) to (g) are repeated several times in order to form alternating layers of tungsten and layers containing tungsten carbides.

71. Process in accordance with claim 70, [*characterised*] characterized in that it is conducted at reactor pressure 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

72. Process in accordance with claim 70, [*characterised*] characterized in that, before the application of a coating to materials or items made from materials selected from a group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys containing titanium, a coating is applied to them consisting of materials which are chemically resistant to hydrogen fluoride, namely nickel, cobalt, copper, silver, gold, platinum, iridium, tantalum, molybdenum and alloys, compounds and mixtures of these, by electrochemical or chemical [*precipitation*] deposition from aqueous solutions, electrolysis of melts or physical and chemical [*vapour precipitation*] vapor deposition.

73. Process in accordance with [any of] claim[s] 70[to 72], [*characterised*] characterized in that the coating is deposited onto friction assemblies.

74. Process in accordance with [any of] claim[s] 70[to 72], [*characterised*] characterized in that the coating is deposited onto a forming tool used for processing materials by means of pressing.

75. Process in accordance with [any of] claim[s] 70[to 72], [*characterised*] characterized in that the coating is deposited onto units of machines and mechanisms operating with compressed gases and liquids or of other pneumatic or hydraulic systems.

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87. Material in accordance with [any of] claim[s] 76[to 86], [*characterised*] characterized in that the said carbide layers additionally contain tungsten.

88. Material in accordance with [any of] claim[s] 76[to 86], [*characterised*] characterized in that the said carbide layers additionally contain carbon.

89. Materials according to [any of] claim[s] 76[to 88], [*characterised*] characterized in that the thickness of its layers ranges from 2 to 10 μm and the ratio of the thicknesses of the alternating layers ranges from 1:1 to 1:5.